# DILUTE SULFURIC ACID PRETREATMENT FOR CELLULOSE RECOVERY FROM SAWDUST

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# ABSTRACT

Cellulose has much function in producing valuable product such as bio-ethanol that has the same function with the crude oil and produce using cheaper and abundant raw material (biomass). The biomass that has been used in this research is sawdust. In order to recover cellulose from sawdust, it is necessary to treat the sawdust using dilute sulfuric acid pretreatment as to remove the lignin and hemicelluloses that bonding the cellulose structure. Compared with the untreated sawdust, 3.4 g/l glucose was dissolved from the cellulose, whereas hemicelluloses which are xylose and arabinose in pre-treated sawdust decreased to 2.5 g/l and 6.8 g/l, respectively. The results of infrared spectra (IR) and scanning electron microscope (SEM) analysis also showed that the structure and the surface of the sawdust were changed through pretreatment and crystalline cellulose in sawdust pre-treated was disrupted. The maximum cellulose recovery of sawdust was achieved at a sulfuric acid concentration of 4 % and pretreatment time of 120 minutes.

# ABSTRAK

Terdapat pelbagai kegunaan selulosa seperti bio-etanol, yang mempunyai fungsi yang sama dengan minyak mentah, dan boleh dihasilkan daripada bahan mentah yang murah seperti biojisim. Bahan mentah yang digunakan dalam kajian ini adalah sisa habuk kayu gergaji. Untuk mendapatkan selulosa daripada sisa habuk kayu gergaji, sisa habuk kayu gergaji mestilah di rawat menggunakan prarawatan asid sulfurik cair bagi menyingkirkan lignin dan hemiselulosa daripada ikatan struktur selulosa. Perbandingan antara sisa habuk kayu gergaji yang dirawat dengan yang tidak dirawat adalah 3.4 g/l telah larut daripada selulosa kepada glukosa manakala hemiselulosa iaitu xilosa dan arabinosa menurun sebanyak 2.5 g/l dan 6.8 g/l. Keputusan analisa daripada spektrum infra merah (FTIR)  dan imbasan mikroskopi electron (SEM) menunjukkan perubahan struktur dan permukaan sisa habuk kayu gergaji selepas prarawatan dan selulosa kristalin dalam serbuk gergaji prarawatan terganggu. Penghasilan maksimum selulosa daripada habuk kayu gergaji pada kepekatan asid sulfurik cair 4% dan masa prarawatan 120 minit.

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| | |
|---|---|
| *°C* | Celcius |
| *HPLC* | High performance liquid chromatography |
| $H_2SO_4$ | Sulfuric acid |
| *FTIR* | Fourier transform infrared |
| *SEM* | Scanning electron microscopy |
| *NaOH* | Sodium hydroxide |

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# CHAPTER 1

# INTRODUCTION

## 1.1 Background of study

Nowadays, ethanol has higher demand because it use as a vehicles fuel because of the environment problem in recent years. Lignocelluloses such as cellulose, hemicelluloses and lignin are usually use as a raw materials in the production of ethanol. Lignocelluloses biomass is believed to be less expensive and more plentiful than either starch or sucrose containing feedstock. If the materials such as forest residues like sawdust and wood bark, agricultural residues like corn stover or herbaceous grass like switch grass as well as municipal waste are used as feedstock, lignocelluloses based bio-fuels could replace about 30% petroleum currently consumed by the USA. Forest biomass such as sawdust and wood bark are believed to be one of the most abundant sources of sugars, although much research has been reported on herbaceous grass such as switch grass, agricultural residue such as corn stover and municipal waste (Hu *et al*., 2008).

Besides that, the polysaccharides which are cellulose and hemicelluloses present in the lignocelluloses biomass need to be hydrolyzed with acids or enzymes in order to produce fermentable sugars. In many processes in the enzymatic conversion of lignocelluloses biomass to ethanol and other chemical products, a pretreatment stage is required to break the lignin structure and to partially solubilize the polysaccharides (Camassola and Dillon, 2008). Cellulose is a linear polymer of glucose in plant and woody materials. It is contains with hemicelluloses, other structural polysaccharides and surrounded by a lignin seal. Lignin is a complex 3-

dimensional polyaromatic matrix that forms a seal around cellulose micro fibrils and exhibits limited covalent associated with hemicelluloses. This prevents enzymes and acids from accessing some regions of the cellulose polymers (Weil *et al*., 1994).

Pretreatment is an important tool for practical cellulose conversion processes. Pretreatment is required to alter the structure of cellulosic biomass to make cellulose more accessible to the enzymes that convert the carbohydrate polymers into fermentable sugars. Pretreatment also has great potential for improvement of efficiency and lowering of cost through research and development (Mosier *et al*., 2004). Several pretreatment methods such as steam explosion, solvent extraction, and thermal pretreatment using acids or bases and also biological pretreatments have been widely investigated. Otherwise, many pretreatment processes require expensive equipment and large quantities of energy (Camassola and Dillon, 2008). Dilute acid pretreatment has been widely investigated. This is because it is effective and inexpensive among all the pretreatment methods. Beside it can improve cellulose conversion; it also can effectively solubilize hemicelluloses into monomeric sugars and soluble oligomers (Sun and Cheng, 2004).

## 1.2 Problem Statement

As we know, the waste of wood such as sawdust was abundant in Malaysia. This is because in Malaysia, many products from wood such as furniture, papers, and houses. The abundant of the sawdust can increase the pollution of the environment. Furthermore, cellulose cannot biodegradable by mammalian digestive enzymes because it has very long chain and complex structure. It will take a long time to biodegradable so it consider as a non biodegradable.

## 1.3 Research Objectives

The objective of this research is to study the recovery of the cellulose from the sawdust.

## 1.4 Scope of Study

In order to achieve the objective of the research study, several scope of study has been identified such as to study the effects of parameters which are $H_2SO_4$ concentration and residences time for dilute acid pretreatment process. Besides that, to investigate the cellulose, hemicelluloses and lignin composition in sawdust using Fourier Transform Infrared (FTIR) and Scanning Electron Microscopy (SEM) and to analyze the monomer sugars using High Performance Liquid Chromatography (HPLC).

## 1.5 Significant of the Study

In using of sawdust as a raw material can consider as a low cost because sawdust was abundant and inexpensive in Malaysia. Otherwise, the composition of the cellulose is plenty in sawdust. The food industry, medical industry and also chemical industry can get more profit because of the inexpensive of the sawdust. The reuse of the sawdust also can reduce the pollution of the environment. Besides that, the production of cellulose has a potential in a future because from the cellulose, many valuable product can be produce such as a bio-ethanol which is the fuel that has same function with the crude oil like petrol but the bio-ethanol has a lower cost and lower price than it. Besides that, the production of sorbitol also one of the products from cellulose. Sorbitol has higher demand because it widely used in the food industry, not only as a sweetener but also as a humectants, texturizer, and softener. Its caloric value is similar to glucose, but it is less capable of causing hyperglycemia because it is converted to fructose in the liver. Other sorbitol applications include pharmaceutical, cosmetic, textile, and paper goods.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Introduction

Lignocelluloses biomass is mainly composed of cellulose, hemicelluloses and lignin. In enzymatic hydrolysis, cellulose was hydrolyzed to its monomeric constituents and then fermented to ethanol or other products. Otherwise, the network between lignin-hemicelluloses were embedded cellulose fibers was slow the cellulose biodegradation by cellulolytic enzymes. Because of that, pretreatment process is important to remove the protecting shield of lignin-hemicelluloses, and make the cellulose that produce is suitable for enzymatic hydrolysis (Esteghlalian *et al*., 1996).

Otherwise, the lignocellulosic feedstock was very effective raw material because it can reduce the cost production of ethanol because it is less expensive and also available in large quantities (Silverstein *et al*., 2007).

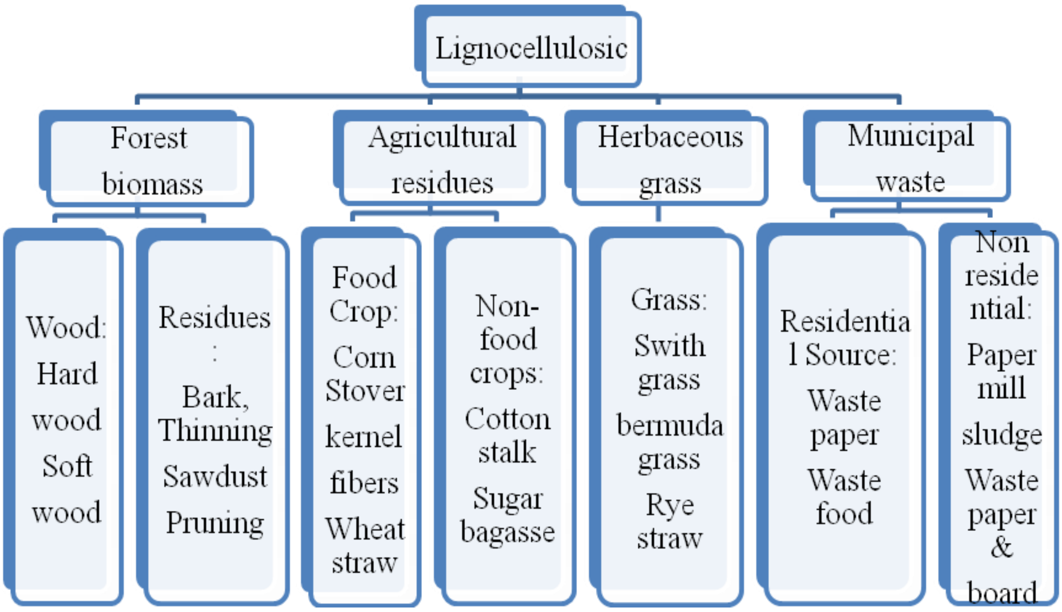


**Figure 2.1 :** Sources of Lignocellulosic.

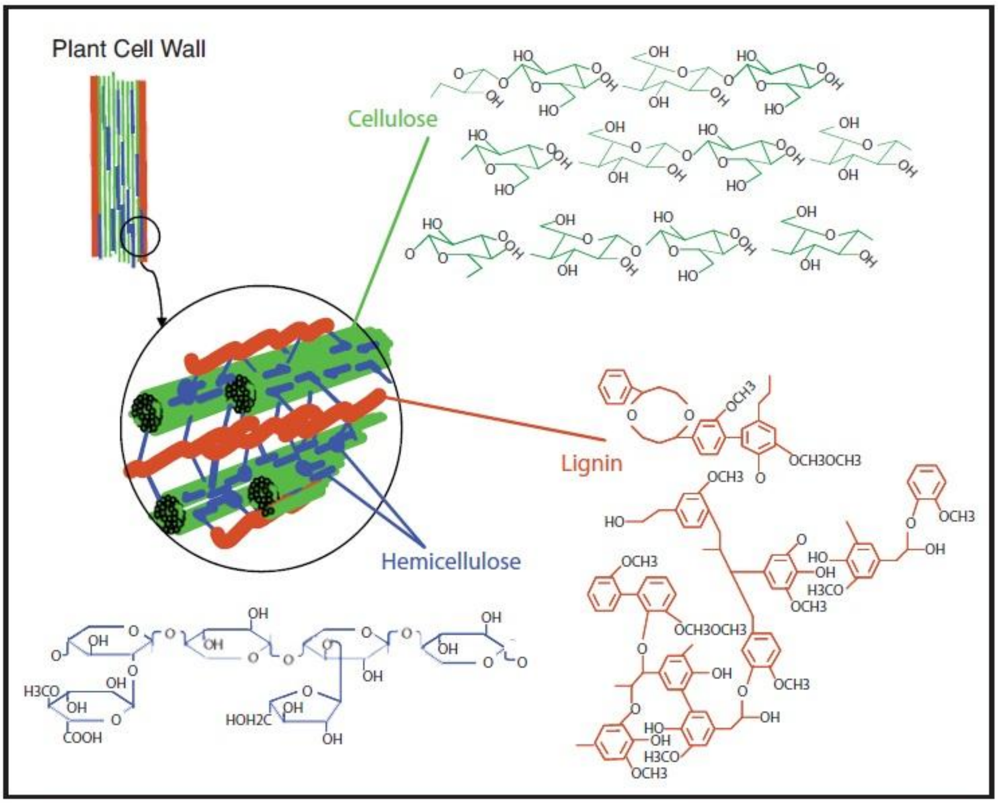


**Figure 2.2 :** Structure of cellulose, hemicelluloses, and lignin.

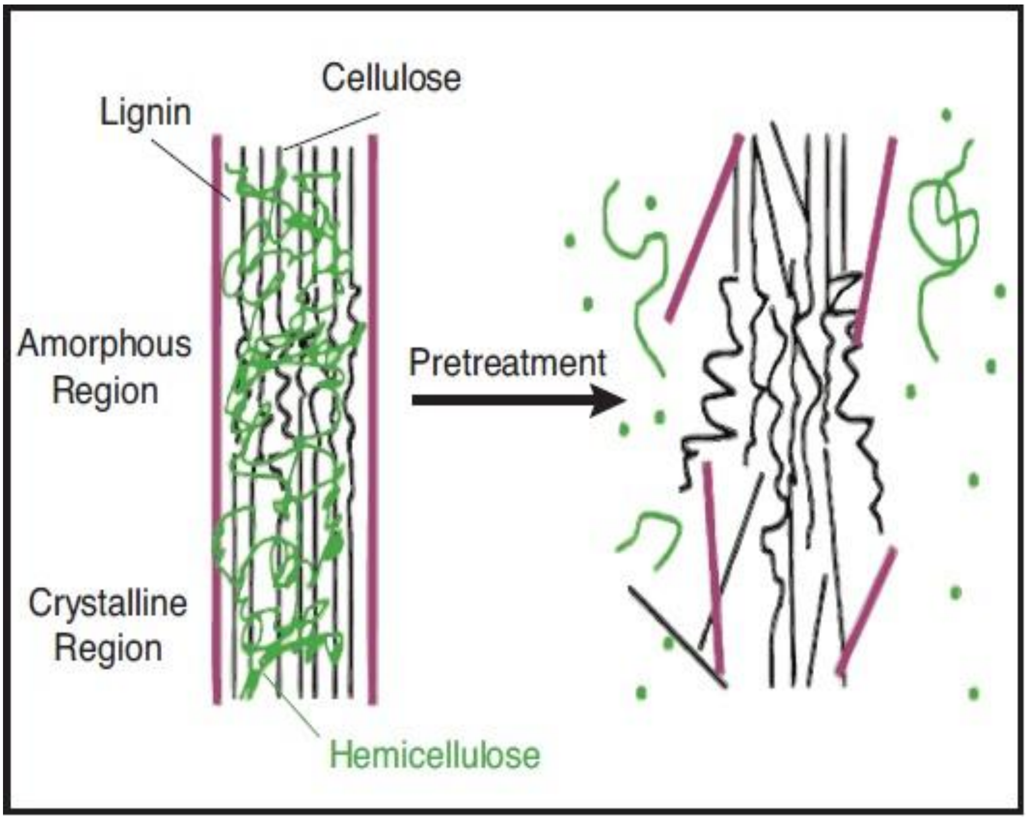


**Figure 2.3 :** Schematic of goals of pretreatment on lignocellulosic material.

Many ways of pretreatment process such as physical treatment like a high energy radiation, steam explosion and ball milling, chemical treatment with acid or basic catalysts, and biological treatments. Pretreatment can affect the structure of biomass by solubilizing or otherwise altering hemicelluloses, altering lignin structure, reducing cellulose crystallinity and increasing the available surface area and pore volume of the substrate. During pretreatment, hemicelluloses may be hydrolyzed to their monomeric constituents and lignin- hemicelluloses-cellulose interactions partially disrupted (Esteghlalian *et al*., 1996).

## 2.2 Raw material for recovery cellulose.

There are several feedstocks for recovery cellulose which is starch, corn stover, wheat straw, sugar bagasse that are among the agricultural residues. Table 2.1 show the percent dry weight composition of lignocelluloses in biomass feedstock.

**Table 2.1 :** Percent dry weight composition of lignocelluloses.

| Feedstock | Glucan (cellulose) | Xylan (hemicellulose) | Lignin |
|---|---|---|---|
| Corn stover[a] | 37.5 | 22.4 | 17.6 |
| Corn fiber[b,c] | 14.28 | 16.8 | 8.4 |
| Pine wood[d] | 46.4 | 8.8 | 29.4 |
| Popular[d] | 49.9 | 17.4 | 18.1 |
| Wheat straw[d] | 38.2 | 21.2 | 23.4 |
| Switch grass[d] | 31.0 | 20.4 | 17.6 |
| Office paper[d] | 68.6 | 12.4 | 11.3 |

Lignocellulosic complex is the most abundant biopolymer in the Earth. It is considered that lignocellulosic biomass comprises about 50% of world biomass and its annual production was estimated in 10–50 billion ton. Many lignocellulosic materials have been tested for bioethanol production as observed. In general, prospective lignocellulosic materials for fuel ethanol production can be divided into six main groups: crop residues such as cane bagasse, corn stover, wheat straw, rice straw, rice hulls, barley straw, sweet sorghum bagasse, olive stones and pulp, hardwood such as aspen and poplar, softwood such as pine and spruce, cellulose wastes such as newsprint, waste office paper and recycled paper sludge, herbaceous biomass such as alfalfa hay, switchgrass, reed canary grass, coastal Bermudagrass and thimothy grass.

**Figure 2.4 :** Sugarcane crop for feedstock of recovery cellulose.

**Figure 2.5 :** Corn stover as a raw material for recovery cellulose.

**Figure 2.6 :** Rice straw as a feedstock of recovery cellulose.

**Figure 2.7 :** Cellulosic waste use as a raw material for recovery cellulose.

Nowadays, the forest product industry was discarded large quantities of cellulosic waste products because they cannot be utilized as food for man in their present forms. Besides that, woody biomass such as sawdust was containing 70 to 80% carbohydrates. Furthermore, woody biomass has physically larger and structurally stronger and denser and also has higher lignin content (Zhu and Pan, 2009). Besides that, sawdust from hardwood has high lignin and low intracellular nutrient content than softwood sawdust. Because of that, only a small percentage of these carbohydrates can be utilized by the ruminant (Keith and Daniels, 1976).

**Figure 2.8 :** Sawdust from sawmill.

**Figure 2.9 :** Hardwood sawdust for cellulose recovery.

Sawdust is a waste by-product of the timber industry that is either used as cooking fuel or a packing material. It is composed of three important constituents such as cellulose, lignin, and hemicelluloses. Sawdust is not only abundant, but also it is actually an efficient adsorbent that is effective to many types of pollutants, such as dyes, oil, salt and heavy metals. Many agricultural by-products are little or no economic value, and some, such as sawdust, which are available in large quantities in lumber mills, are often present a disposal problem (Pekkuz, 2007).

## 2.3 Cellulose (Product)

In herbaceous and woody plants, cellulose exists as a linear polymer of glucose. Besides that, cellulose also associated with another polysaccharide, hemicelluloses and seal with lignin which is a complex three dimensional polychromatic compound that is resistant to enzyme and acid hydrolysis (Weil *et al*., 1998).

Cellulose exists of D-glucose subunits, linked by b-1, 4 glycosidic bonds. In plant consists two part of cellulose which is organized part that contain a crystalline structure and another part is not well organized that contain amorphous structure. Cellulose fibrils or cellulose bundles were the cellulose strains that ‘bundled’ together. These cellulose fibrils are mostly independent and weakly bound through hydrogen bonding (Hendriks and Zeeman, 2008).

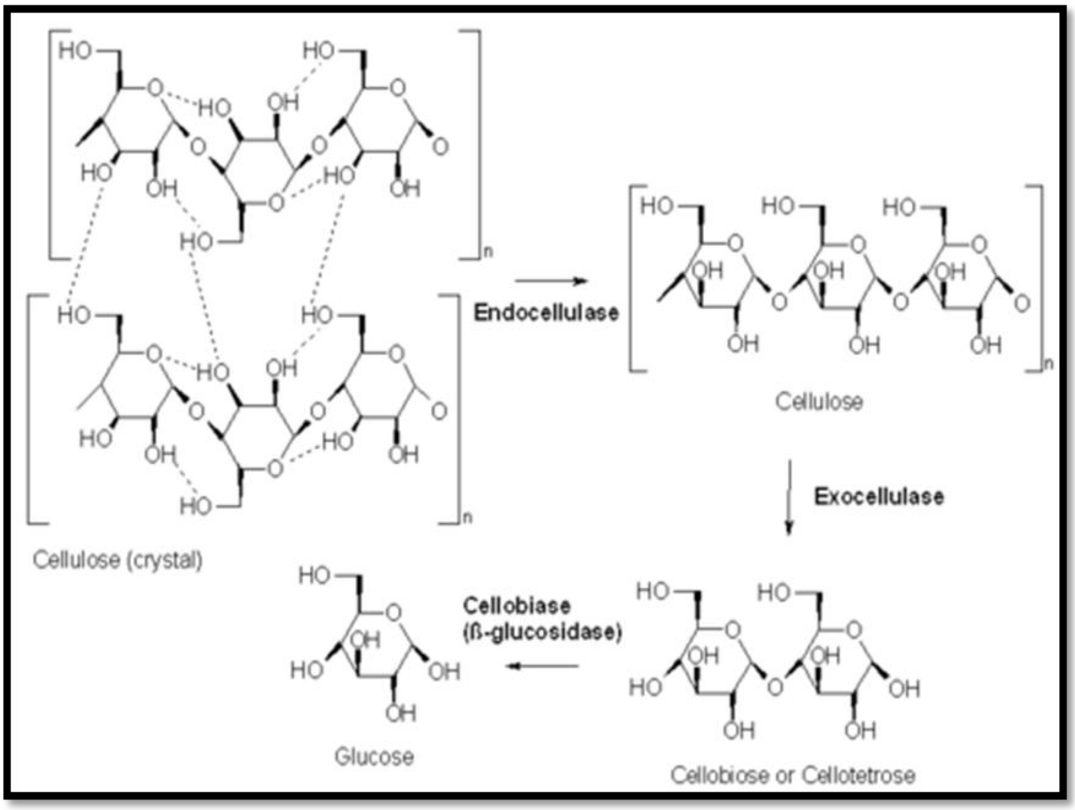


**Figure 2.10 :** Structure of Cellulose.

Cellulose, like starch, is a polymer of glucose. However, unlike starch, the specific structure of cellulose favors the ordering of the polymer chains into tightly packed, highly crystalline structures that is water insoluble and resistant to depolymerization (Mosier *et al*., 2005). Besides that, cellulose can be enzymatically hydrolyzed to its monomeric constituents (glucose units) and then fermented to ethanol or other products (Esteghlalian *et al*., 1997).

## 2.4 Pretreatment Process

In general, pretreatment can be classified into biological pretreatment, physical pretreatment and also chemical pretreatment according to the different force or energy consumed in the pretreatment process. Some pretreatment combines any two or all of these pretreatment and can be produce subcategories. Biological pretreatment has not attached much attention, probably because of kinetic and economic considerations; although there have been various researches showing biological pretreatment can be an effective way to recover sugars from different species of biomass.

Physical and chemical pretreatments have been the subject of intensive research. Steam and water are usually excluded from being considered as chemical agent for pretreatment, since no extra chemical are added to the biomass. Physical pretreatment include comminution, in which the particle sizes of the biomass are reduced with mechanical forces, steam explosion, and hydrothermalysis.

Acids or bases promote hydrolysis and improve sugar recovery yield from cellulose by removing hemicelluloses or lignin during pretreatment. Sulfuric acid and sodium hydroxide are the most commonly used acid and base, respectively. Another approach of for pretreatment is to use liquid formulations capable for acting as solvent for cellulose. Work with cellulose solvent systems has shown the enzymatic hydrolysis could be greatly improved, but the work mainly has been restricted to agricultural residues and herbaceous grass.

Little has been reported about the use of cellulose solvents in pretreating forest biomass such as wood, bark, or mixtures of such residue. A broad range of chemical pretreatment, such as concentrated mineral acids which is sulfuric acid and hydrochloric acid, ammonia based solvent, aprotic solvents, as well as wet oxidation also reduce cellulose crystalline, disrupt the association of lignin with cellulose, and dissolve cellulose. However, the economics of these methods do not permit any practical application when compared to the value of glucose. Lime pretreatment and ammonium pretreatment have seemed to be the most attractive alkaline pretreatment, while most attention in acid pretreatment has been concentrated on the use of sulfur